

Ab-initio modeling of an anion C_{60}^- pseudopotential for fullerene-based compounds.

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Abstract. A pseudopotential of C_{60}^- has been constructed from *ab-initio* quantum-mechanical calculations. Since the obtained pseudopotential can be easily fitted by rather simple analytical approximation it can be effectively used both in classical and quantum molecular dynamics of fullerene-based compounds.

1 Introduction

Fullerene C_{60} is the most studied and widely used among all fullerenes because of the availability, high symmetry and low price [1]. Some of the most promising fields of application of these novel materials are artificial photosynthesis, non-linear optics and the preparation of photoactive films and nanostructures (see, for example [2]). Because of high electron affinity and small rearrangement energy fullerenes, in particular C_{60} , play a role of electron-acceptors in such systems and produce very stable radical pairs. In particular, it was demonstrated that a π -conjugated polymer was able to efficiently transfer electrons to the C_{60} core giving rise to long-lived charge-separated states. For example the donor-acceptor compound $[C_{60}]PCBM$ [3] is the most known and effectively used in organic solar photoelectric cells for the last time. But, due to the difficulties in the modeling extended and possible nanostructured materials as $[C_{60}]PCBM$ an isolated molecular limit is preferable, so the investigations of the isolated anions and radical anions of fullerenes, in particular C_{60}^- , seems to be actual.

The anions and radical anions of fullerenes have been an object of intensive investigations during last two decade [1, 4, 5]. The anionic fullerenes have been observed in ion cyclotron resonance traps [6], storage rings [7] and electrospray mass spectrometry [8]. The theoretical systematic study of the stability of highly charged anionic fullerenes has been performed within different levels of theory [9, 10]. But for the developing efficient quantum simulation methods, which allow us to predict the optimized geometry of the fullerene C_{60} compounds with reasonable computer cost and accuracy, we suggest to construct a pseudopotential of C_{60}^- .

The recent calculations showed that the application of simple and widely used jellium model doesn't bring data into accordance with results of more complicated but ac-

curate *ab-initio* calculations [11]. In this paper the pseudopotential of C_{60}^- has been constructed on the basis of the total electrostatic potential of C_{60}^- calculated within the *ab-initio* approach.

The atomic system of units, $m = |e| = \hbar = 1$, is used throughout the paper.

2 Method of calculation

2.1 Ab-initio calculations

All *ab-initio* computations are performed by using the FireFly QC package [12]. For the first the fully optimized geometry and the total energy of C_{60}^- have been obtained from the Hartree-Fock and density functional theory (DFT) calculations by ROHF/6-31G(d) and B3LYP/6-31G(d) levels respectively. Then within the optimized geometry the *ab-initio* calculations of the electronic structure and the total charge density of C_{60}^- have been performed at the same levels of theory, which is shown to provide reasonable results for small carbon clusters [13] and fullerenes [10, 14], both charged and neutral. Although the inclusion of diffuse functions is usually important to obtain accurate absolute energies for anions, it has recently been shown that the 6-31G(d) and 6-31G+(d) basis sets give similar results for geometries, charge distributions, and relative energies of anionic C_{60} and C_{70} fullerenes [15, 16].

The important point of the *ab-initio* calculations of the total charge density is to apply the corresponding key in the input of the FireFly program like $AIMPAC = 1$ to obtain the practical information about molecular orbital wave functions which are used in the next step of construction of the pseudopotential of C_{60}^- .

2.2 Pseudopotential construction

The pseudopotential of C_{60}^- can be constructed on the basis of the total electrostatic potential. The latter is presented as a sum of two summands: the potential of nuclei $U_n(\mathbf{r})$, which depends on positions of sixty carbon atoms, and the potential created by electron density $\rho(\mathbf{r})$ of 361 electrons $U_{el}(\mathbf{r})$:

$$U_{tot}(\mathbf{r}) = U_n(\mathbf{r}) + U_{el}(\mathbf{r}) = - \sum_{i=1}^{60} \frac{6}{|\mathbf{r} - \mathbf{R}_i|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' . \quad (1)$$

The positions of the carbon atoms within the optimized geometry and corresponding charge density have been extracted from results of the *ab-initio* FireFly QC package calculations by using of a Multifunctional Wavefunction Analyzer (Multiwfn) [17] (see for example a color filled map of the electron charge density of the C_{60}^- obtained from *ab-initio* calculations prepared within the Multiwfn [17] software on the Fig. 1). This software has been then used for computation of the corresponding electrostatic potentials on a specified grid of the position vector \mathbf{r} . After that we have averaged the electrostatic potential obtained from Multiwfn software over the directions of the position vector \mathbf{r} to construct the radial dependence of C_{60}^- pseudopotential $U_{pseudo}(r)$ and to obtain averaged electron density $\bar{\rho}(r)$:

$$\begin{aligned} U_{pseudo}(r) &= \bar{U}_{tot}(r) = \bar{U}_n(r) + \bar{U}_{el}(r) , \\ \bar{U}_i(r) &= \frac{1}{4\pi} \int U_i(\mathbf{r}) d\Omega \quad (i = tot, n, el) , \\ \bar{\rho}(r) &= \frac{1}{4\pi} \int \rho(\mathbf{r}) d\Omega . \end{aligned} \quad (2)$$

3 Results

For the first we have checked the non-applicability of the jellium model for purpose of construction of pseudopotential of C_{60}^- . The averaged radial valence electron density $\bar{\rho}(r)$ of C_{60}^- calculated by *ab-initio* method has been compared with results of the jellium model and *ab-initio* calculations for C_{60} [11]. The Hartree-Fock method has been used for self-consistent calculations in all three cases. Fig.2 demonstrates the density profiles of valence electrons of C_{60} [11] and C_{60}^- (present work, ROHF/6-31G(d) level) as a function of radial distance from a center of fullerene. As Fig.2 indicates, the results of *ab-initio* calculations for fullerene and anion are close, but substantially differ from the results of jellium model calculations for C_{60} , which makes this approach non applicable to solving a problem of determination of C_{60}^- pseudopotential.

The results of the C_{60}^- pseudopotential calculations by Hartree-Fock method (ROHF/6-31G(d)) and within DFT

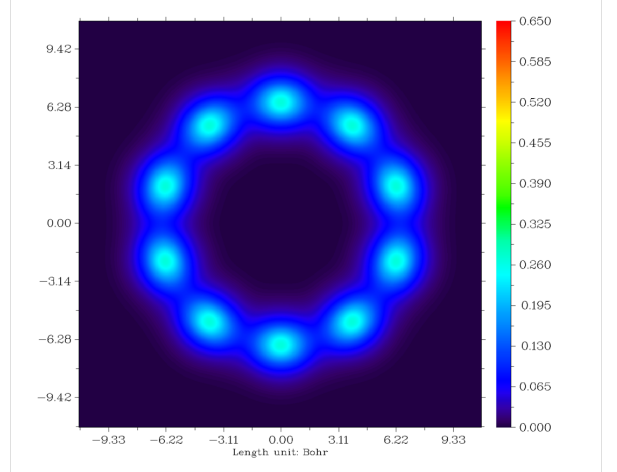


Fig. 1. A color filled map of the electron charge density of the C_{60}^- obtained from *ab-initio* calculations prepared within the Multiwfn [17] software in the plane X,Y. The origin of the X,Y,Z is set at the center of C_{60}^- , lengths unit is Bohr.

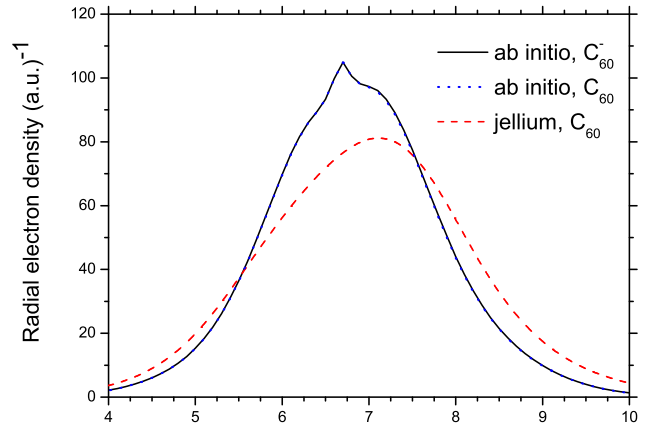


Fig. 2. Radial valence electron density of C_{60}^- (ROHF/6-31G(d) level, solid line) is compared with the same of C_{60} calculated by *ab-initio* method [11] (ROHF/6-31G(d) level, blue dotted line) and with use the jellium model [11] (red dashed line).

(B3LYP/6-31G(d)) are presented and compared in Fig.3. Note that the usage of the different approaches for the electronic structure calculations leads to the significant discrepancy of the corresponding one-particle energies results but doesn't lead to the any noticeable differences in the resulting behavior of pseudopotential (compare blue and red solid line in Fig.3).

It should be mentioned several important features of the pseudopotential obtained. The first one is the correct asymptotic behavior at the large distances as $1/r$, which is

typical for a single negative ion (see Fig.3). The numerical analysis shows that the pseudopotential behavior begins to satisfy the $1/r$ law at the radial distance about 10 a.u. Secondly the pseudopotential demonstrates two different types of interaction between the fullerene's anion and an external electron: the strong attraction close to a radius of fullerene's anion and the weak repulsion outside and inside of fullerene cage. This combination of repulsion and attraction gives rise the weak barriers for an any negative projectile particle and can lead to increasing of probability for the projectile to "getting stuck" on the fullerene cage.

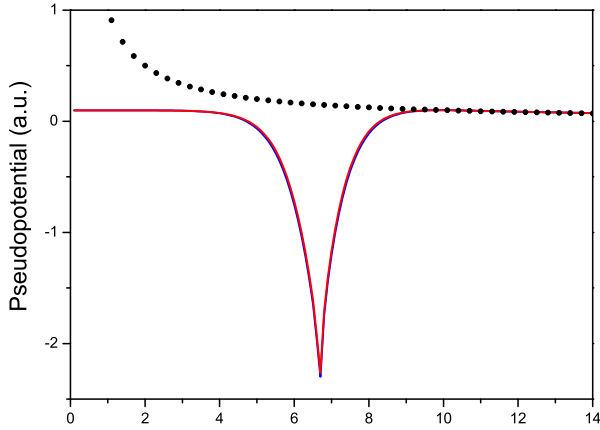


Fig. 3. Pseudopotential of C_{60}^- obtained from *ab-initio* calculations: ROHF/6-31G(d) (blue solid line), B3LYP/6-31G(d) (red solid line) and compared with an $1/r$ asymptotic behavior (black dots).

For purposes of the classical and quantum molecular dynamics of fullerene-based compounds it is reasonable to make the analytical approximation of the numerically obtained pseudopotential. Within the range 0 – 10 a.u. of radial distance the pseudopotential has been approximated by sum (3) of constant and Chesler-Cram single peak function (see Fig.4). This Chesler-Cram function [18] is applied to approximate experimental results in the processing of chromatographic data. We use this function because it may describe discontinuity point and consists of elementary functions. The general view of our function is presented by the following formula:

$$u(r) = y_0 + A[e^{-\frac{(r-r_{c1})^2}{2w}} + Be^{-\frac{1}{2}k_3(|r-r_{c3}|+(r-r_{c3}))} \times (1 - 0.5(1 - \tanh(k_2(r - r_{c2}))))], \quad (3)$$

where r is the radial distance, y_0 , A , r_{c1} , w , B , k_2 , r_{c2} , k_3 , r_{c3} are approximation constants. The array of constants that allows to achieve the best result is represented in the table 1.

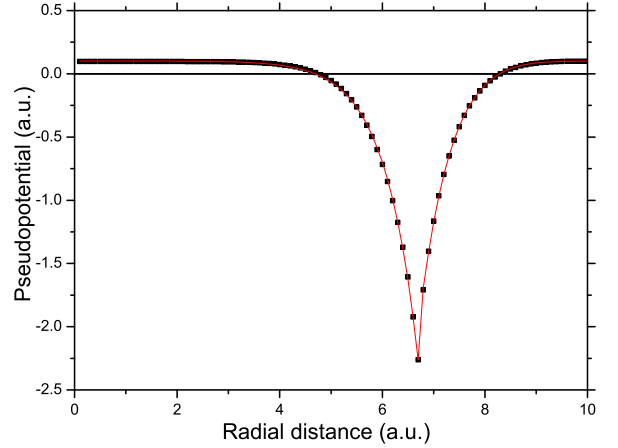


Fig. 4. Approximation (red solid line) of the pseudopotential of C_{60}^- obtained from *ab-initio* B3LYP/6-31G(d) calculations (black dots).

Table 1. array of constants

<i>symbol</i>	<i>value</i>
y_0	0,10096
r_{c1}	6,66092
A	-1,60691
w	$4,0523 * 10^{-4}$
k_2	0,79686
r_{c2}	8,32747
B	20,83852
k_3	3,14767
r_{c3}	6,66996

4 Conclusion

In this work we have constructed the pseudopotential of the fullerene anion C_{60}^- for molecular dynamic purposes. The method of construction is based on the using of the charge density obtained by the *ab-initio* calculations and on the averaging of the corresponding total electrostatic potential to make the radial dependence of the pseudopotential.

The pseudopotential of the fullerene anion C_{60}^- obtained has rather simple analytical approximation and then can be effectively used both in classical and quantum molecular dynamics of fullerene-based compounds.

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